ELASTIC MODULUS IN RIGID Al₂O₃/ZrO₂ CERAMIC LAMINATES

J.S. Moya¹, J.A. Sánchez-Herencia¹*, J.F. Bartolomé¹ and T. Tanimoto²
¹Instituto de Ciencia de Materiales de Madrid (ICMCM), CSIC, Cantoblanco,
Madrid, Spain
²Shonan Institute of Technology (SIT), Fujisawa, Kanagawa, Japan

(Received February 17, 1997)
(Accepted May 29, 1997)

Introduction

Layered ceramics have recently attracted a great deal of interest because of their better capability to tailor materials with anisotropic properties to satisfy the complex requirements of emerging technologies (1), such as the electronics and microelectronics industry (2-5) and structural applications (6-14). Particularly, Zirconia-based composite ceramics have received most attention due to the possibility of improving mechanical properties by microscopic effects including a stress-induced transformation of the metastable tetragonal inclusions and microcracking around the unstabilized monoclinic inclusions (15,16), or by interfacial mechanisms acting at a macroscopic scale in multilayer composites. Internal stresses, developed as a consequence of the different thermal contractions in laminated zirconia-based materials, provoke a deviation of the propagating cracks at the interface, and so an improved toughness is obtained for these materials (17-19). Recent studies have shown that multilayered composites of Al₂O₃ and Ce-ZrO₂ exhibit especially high fracture toughness because of the influence of the laminar microstructure on the shape of the crack tip transformation zone (20).

It is well known that many transformation-toughened zirconia-based ceramics exhibit an increase in strength after surface grinding. This strength increase is attributed to the increase in volume which occurs because of the tetragonal → monoclinic transition in zirconia particles in the near surface regions. Specially, upon transformation to the monoclinic polymorph, the surface region suffers a net increase in volume which is constrained by the bulk. As a result, large surface compressive stresses are developed, leading to an enhancement in strength. Stresses as high as 1 GPa have been measured experimentally (21). A surface-compression-strengthened ceramic can be considered to be a toughened ceramic since the resistance to fracture from a surface crack is enhanced by the presence of the surface compression (22). The enhanced fracture toughness must be viewed as an apparent extrinsic fracture toughness since higher resistance to fracture is derived from a reduction of the crack-driving force rather than an increase in the intrinsic resistance to crack extension (23).

In previous works (24-27), it has been shown that by making a three-layer composite in which the central region contains the matrix oxide and stabilized zirconia and the surface layers contain the matrix

*Present address: Materials Dept., UC-Santa Barbara, CA 93106, USA

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oxide and unstabilized zirconia, strength can be substantially enhanced relative to the monolithic materials containing the oxide matrix and either stabilized or unstabilized zirconia. The magnitude of the surface compressive stresses can be varied controlling the thickness of the outer layers and by proper thermal treatment in which the relative amounts of the monoclinic and tetragonal phases in the outer layers are controlled or by varying the volume fraction of total zirconia in the component. Often, the residual stresses are tailored to obtain high surface compression and a moderate bulk tension.

In the present investigation, we have studied the effects of macroscopic residual stresses on stress intensities in the different layers of the Al$_2$O$_3$/ZrO$_2$ laminates and the influence of the layered design on the elastic modulus of these materials.

**Experimental Procedure**

The following starting materials have been used: Al$_2$O$_3$ (Condea HPA 0.5 Germany) with $d_0 = 0.5 \, \mu\text{m}$, specific surface area of 9.5 m$^2$/g and 99.9% purity; monoclinic ZrO$_2$ (Dynamit Nobel, Germany) with $d_0 = 1 \, \mu\text{m}$ and specific surface area of 66.7 m$^2$/g and tetragonal ZrO$_2$ (3 mol% Y$_2$O$_3$) (TZ-3YS Tosoh Japan) with $d_0 = 0.4 \, \mu\text{m}$ and specific surface area of 6.7 m$^2$/g.

Stable aqueous suspensions of Al$_2$O$_3$, Al$_2$O$_3$ + 15 vol% m-ZrO$_2$ and Al$_2$O$_3$ + 15 vol% t-ZrO$_2$ (Y$_2$O$_3$) with 70 wt% solid load were prepared by adjusting the pH with HCl to a value of 4 [28]. The rheological properties of the different slips were studied using a rotational viscometer (Haake Rotovisco

![Flow chart of the experimental procedure.](image)
HV20) at a constant temperature of 25°C. Monolithic and laminated dense (>99% th.) composites were obtained following the flow chart of Figure 1.

The thermal expansion behavior of different monolithic and laminated sintered materials between room temperature at 1400°C during heating and cooling was established in a dilatometer (Adamel Lhomargy, Ivry, France) with alumina support. The differential thermal analysis (DTA) was performed in a Netsch STA-409 using a constant heating rate of 10 K/min and solid sintered specimens of approximately the same weight (0.8-0.9 g) for each composition.

Flexural strength test sample bars with 40 × 4 × 2 mm dimensions were cut from the fired plates with tensile surfaces oriented parallel to the layers. Surfaces were polished successively with 9, 6 and 1 μm diamond paste and the edges were rounded during polishing operation. Four-point bend strength tests were conducted with upper and lower spans of 9.5 and 19 mm respectively and a crosshead speed of 0.5 mm/min.

The dimensions of beams for tensile test were approximately 50 × 4 × 1 mm. Tensile tests were performed with a specially designed specimen geometry (29) as shown in Figure 2. The mechanical properties were evaluated using an Instron 4206 testing machine. The specimens were loaded to failure with a cross-head speed of 0.5 mm/min. In general, tension testing of ceramic specimens is quite difficult to perform because the fracture can occur easily at the gripping area. This is due to the inherent low fracture toughness of most ceramic specimens. In the present work, an attempt was made to evaluate the tensile strength properties of the samples with a specially designed specimen geometry. In this method, tabs were bonded to both sizes of the plate to prevent the fracture at this area. The tabs have a taper in order to reduce stress concentrations at the gripping area. The material selected for the end tabs was chopped glass mat reinforced polyester, which is ductile and soft as compared to alumina based ceramics. The stress distribution at the vicinity of the tab was calculated by a finite element method to determine the validity of the adopted specimen geometry (29). Strain gauges were mounted on all testing specimens in two directions, parallel and transverse to the loading direction in order to determine Young’s modulus and Poisson’s ratio.

Results and Discussion

The SEM micrographs of the A/AMZ, ATZ/AMZ cross sections are shown in Figure 3. From the SEM study the average alumina grain size of the A, ATZ and AMZ compacts were found to be 50, 5 and 4 μm

![Figure 2. Dimensions and geometry of the tensile test specimens.](image-url)
respectively, and the average of the zirconia grain size of the ATZ and AMZ were found ≈ 2 µm in both cases. The fraction of tetragonal zirconia in AMZ was determined by Garvie’s equation on the sintered sample surface and was found to be <10%, which is in good agreement with data obtained by other authors in Alumina/ZrO₂ composites with coarse ZrO₂ grains (≥2 µm) (30). As observed the layer thickness in the laminates grade from 110 to 130 µm.

The dilatometric curves corresponding to the monolithic composites are shown in Figure 4. As can be observed the AMZ compact curve exhibits the typical hysteresis due to tetragonal ↔ monoclinic transformation of ZrO₂ particles.

![Figure 3. SEM micrographs corresponding to (a) A/AMZ and (b) ATZ/AMZ cross sections.](image)

![Figure 4. Dilatometrics curves corresponding to monolithic compacts.](image)
TABLE 1

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>AMZ vol.%</th>
<th>ATZ vol.%</th>
<th>A vol.%</th>
<th>σ_f (MPa)</th>
<th>σ_u (MPa)</th>
<th>ν</th>
<th>E (GPa)</th>
<th>E* (GPa)</th>
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<td>A</td>
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<td>100</td>
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<td>90 ± 6</td>
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<tr>
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<td>0</td>
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<td>405 ± 20</td>
<td>0.21 ± 0.01</td>
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<tr>
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<td>0</td>
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<td>23 ± 2</td>
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<tr>
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<td>53</td>
<td>120 ± 15</td>
<td>43 ± 3</td>
<td>0.096 ± 0.007</td>
<td>158 ± 11</td>
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<tr>
<td>ATZ/AMZ</td>
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<td>51</td>
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<td>370 ± 20</td>
<td>209 ± 15</td>
<td>0.21 ± 0.01</td>
<td>374 ± 26</td>
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* Calculated by the rule of mixtures.

In Table 1 the σ_f, σ_u, ν, E values corresponding to monolithic and layered composites are shown. In the case of A/AMZ laminates, the crack pattern observed in the alumina layer (Fig. 3) can be explained considering the high thermal expansion mismatch developed during cooling at 700-650°C temperature range (Fig. 5A). Dilatation takes place as a consequence of the martensitic tetragonal → monoclinic transformation of the coarse zirconia grains. Because of this mismatch (Δε) the residual tensile stress developed in the alumina layer, assuming that the thickness of Al2O3 and Al2O3/ZrO2 layers are similar, can be calculated according to:

\[
\sigma_R = \frac{1}{2} \frac{E}{1-\nu} \Delta \varepsilon
\]

where E is the Young’s modulus of the alumina layer, and ν is the Poisson coefficient. Considering that: Δε = 1.5 × 10^-3 (Fig. 4), E_A = 404 GPa (Table 1) and ν_A = 0.26 (Table 1), the residual tensile stress was found to be σ_R = 410 MPa. This residual stress value justifies the cracking observed in the A/AMZ

Figure 5. Dilatometric curves corresponding to: (A) A/AMZ and (B) ATZ/AMZ laminates.
lamine since the tensile strength of the alumina layer (90 MPa (Table 1)) was largely surpassed. The microcracks developed in the AMZ layers as well as the long perpendicular cracks formed in the alumina layers justify the low \( \sigma_T \) and \( \sigma_L \) values (Table 1) obtained in this laminate. As in the case of the monolithic AMZ the \( v \) value is also depleted by this microcracking phenomenon. The obtained experimental E value was found to be \( \approx 27\% \) smaller than the one calculated according to rules of mixture. This fact is explained because of the cracks introduced during cooling in the alumina layers.

In the case of ATZ/AMZ laminate the experimental value of the elastic modulus (374 GPa) is about 55 % higher than the one calculated according to the rule of mixture (241 GPa). The Poisson's coefficient value was found to be similar to the one measured in the monolithic material without any crack (ATZ). The \( \sigma_T \) was found to be \( \approx 10 \) times and \( \sigma_T = 3 \) times higher than the one corresponding to the A/AMZ laminate. This unexpected behaviour can be explained since no martensitic transformation and

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**Figure 6.** DTA curves showing the endothermic peak corresponding to m-t transformation of zirconia in the case of AMZ and A/AMZ specimens.

**Figure 7.** Vickers indentation cracks patterns in ATZ/AMZ cross-section showing the existence of a tensile residual stress in ATZ layer (a) and compressive residual stress in AMZ layer (b).
consequently no microcracking takes place during cooling in this laminate material as can be observed in the corresponding differential thermal analysis (DTA) and dilatometric curves (Figs. 5B, 6).

The AMZ layers of this laminate are subjected to compressive residual stresses and the ATZ ones to tensile residual stresses as can be deduced from the Vickers indentation cracks pattern shown in Figure 7. These residual stresses can be evaluated considering that cooling t-m of zirconia grains must take place in few localized points of the AMZ layers, then from equation (1) and the obtained values for $E_{ATZ}$ (360 GPa), $\Delta \varepsilon (=1.5 \times 10^{-3})$ and $v_{ATZ}$ (0.21), the calculated value $\sigma_k$ at the ATZ layer was found to be $\approx 341$ MPa. This value is slightly lower than the $\sigma_l$ value (405 MPa) of the monolithic ATZ material (Table 1).

Figure 9. Residual compressive stress at AMZ layer versus layer thickness (a/b) for different $\Delta \varepsilon$ values.
Consequently on cooling the martensitic transformation of the tetragonal to monoclinic zirconia grains dispersed in the AMZ layers was largely inhibited. In the case of AMZ monolithic with a similar average ZrO$_2$ grain size (≈2 μm) almost all the zirconia grains (>90 %) transform on cooling to monoclinic symmetry (Fig. 4). It is worth mentioning that the tetragonal- monoclinic ZrO$_2$ transformation (Δv=$+$4%) in an alumina matrix is grain size dependent (30, 31) as in the case of metals and alloys (32). This particular residual stress field also affects the fracture mode of the laminate (Fig. 8). The crack deflects when it reaches the compressive residual stress field located at AMZ layers. Conversely when the crack passes through the ATZ layers subjected to a residual tensile stress, the fracture mode is transgranular being intergranular when the crack deflects at ATZ/AMZ interface.

The general equation (33):

$$
\sigma_{R} = \frac{\Delta \varepsilon E_{AMZ}}{1-\nu_{AMZ}} \left[ 1 + \frac{a}{b} \frac{E_{AMZ}}{E_{ATZ}} \left( 1 - \nu_{AMZ} \right) \left( 1 - \nu_{ATZ} \right) \right]^1
$$

where $a$ and $b$ are the thickness of the AMZ and the ATZ layers. Since $E_{AMZ}$ (without cracks) = $E_{ATZ}$ and $\nu_{AMZ} = \nu_{ATZ}$ equation (2) can be expressed:

$$
\sigma_{R} = \frac{\Delta \varepsilon E_{AMZ}}{1-\nu_{AMZ}} \left[ 1 + \frac{a}{b} \right]^1
$$

According to this equation (3) it is possible to design laminated materials with different layer thickness and Δε value (=X_{mZrO$_2$}) (Fig. 9) where the compressive residual stress at the AMZ layer can be higher than 1 GPa.

As it is well known that high elastic modulus ceramics can be subjected without cracking to very high compressive stress, i.e. ≈10 times higher than the bending strength (34). Then the results obtained in the present investigation open the possibility to design Al$_2$O$_3$/ZrO$_2$ layered ceramics containing thick layers of ATZ subjected to a very low tensile residual stress and thin layers of AMZ subjected to extremely high (>1 GPa) compressive residual stress. This particular microarchitecture can drastically improve the resistance to crack extension and the mechanical performance of this new family of ceramics.

**Conclusions**

The following conclusions can be drawn:

1. By sequential slip casting ATZ/AMZ laminates have been obtained with an elastic modulus ≈55% higher than the one calculated according to the rule of mixture. This increase has been explained considering that the AMZ layers of this laminate are subjected to compressive residual stresses. Because of this, on cooling the tetragonal → monoclinic martensitic transformation of coarse (≈2 μm) zirconia grains dispersed in the alumina matrix was inhibited. This fact affects the fracture behavior of this laminate: (i) deflecting the crack at ATZ/AMZ interface and (ii) changing the fracture mode from transgranular at ATZ layer to intergranular at AMZ layer.

2. It is now possible to design ATZ/AMZ laminated materials with a high compressive residual stress value (>1 GPa) at the AMZ layer by controlling the content of m- ZrO$_2$ in the AMZ and
the thickness ratio of ATZ and AMZ layers. This fact will beneficially affect the fracture behavior of the laminate composites.

Acknowledgments

The authors gratefully thank A.P. Tom sia and E. Saiz for experimental assistance. This work has been supported by CICYT, Spain, under project number MAT-94-0974.

References